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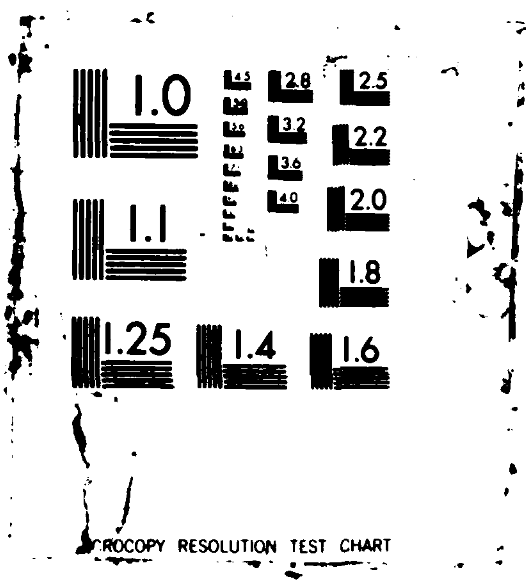
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Initial microstructure studies of multilayer capacitors (MLC)'s have been completed and have shown the presence of a second phase which can be correlated with the "state-switching" phenomena. Most other planned MLC sets embodying a large number of parameter variations have been made and are currently under evaluation. Thermal properties of MLC's have been measured and a heat flow model has been developed to describe temperature changes within the MLC. The dielectric properties of the MLC's have been measured and provide clues as to the origin of the unusual phenomena associated with this material. Instrumentation has been developed for computer-controlled voltage breakdown testing at 77 K.

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[redacted] Bruce L Smith	(202) 767-4907	NP

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CeramPhysics, Inc.
921 Eastwind Drive, Suite #110, Westerville, Ohio 43081 • (614) 882-2231

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Annual Technical Report
AFOSR SBIR Phase II Contract
F49620-86-C-0029

Capacitive Energy Storage at Cryogenic Temperatures

Annual Report: Review of Research

by

C.F. Clark C4C
CeramPhysics, Inc.
Westerville, Ohio 43081

January 23, 1987

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This annual report reviews and summarizes all the work done through Dec. 31, 1986 on the project "Capacitive Energy Storage at Cryogenic Temperatures," AFOSR Contract F49620-86-C-0029. This means that nine months work is being reported since the prime contract was not received until early April 1986.

The early part of the contract has been devoted by the subcontractors, American Technical Ceramics (ATC) and Biggers, Inc. (BI) to a thorough study of the empirical effects of variations in sample manufacturing parameters on breakdown strength. A summary of the analyses completed to date is presented below (Section I) and a review of the status of the other samples is given in Section V.

CeramPhysics, Inc. has spent the first nine months studying the problem of heat flow within multilayer capacitors (Section II), extending basic dielectric measurements on the system of materials (Section III), and preparing equipment and software for measurements at cryogenic temperatures (Section IV). Future plans are given in Section V.

Greater detail on each of these sections is given in the series of quarterly and interim reports which have already been distributed. References will be made in each section to the relevant reports.

I. Microstructural Analysis of Multilayers

From a previous program, nine groups of CPN-17 multilayers had been fabricated by ATC. These had variations in raw niobium source, electrode metal, and dielectric layer thickness and number from group to group. At room temperature there were no significant differences in breakdown voltage among the groups, while at 77 K, one group with a different niobium source showed larger breakdown voltages. There was a strong correlation between <u>geometry</u> and the appearance of the "state-switching" phenomenon, where devices with single thin layers were more likely to switch as were devices with a small transverse electrode pullback and a small active/inactive dielectric ratio. The group with the highest breakdown voltage did not show state-

switching even though the devices were composed of single thin layers. On the other hand this group had a relatively large transverse electrode pullback.

The study of these groups by Biggers, Inc. for this program is entitled "Microstructural Characterization of CPN-17 Multilayer Capacitors." The report examines several aspects of the microstructure of the nine groups of multilayers. Cross-sections of samples were prepared by several different methods and examined with a Scanning Electron Microscope (SEM).

First, "as-fired" surfaces were examined and the only unusual feature was the presence of acicular (needlelike) grains. These probably formed by a change in stoichiometry on the surface during firing, although the possibility remains that these structures are also present in the bulk ceramic and are affecting the breakdown properties. These acicular grains were present in all groups.

Examination of fracture surfaces showed a different result compared to PbO-containing perovskites which normally contain a large intergranular component associated with Pb-rich boundary phase. The absence of this phase in the present samples implies that there is no similar boundary phase in the grains of CPN-17.

In the fracture surfaces there were also some separations of the electrode from the bulk ceramic. These are not present in other samples prepared by other methods and are probably due to a strain between the electrode and ceramic which is released at the time of the fracture. A likely source for the strain is the differential shrinkage rates of the two components during firing. Whatever the source of the strain, it is a possible source of breakdowns especially at the edges of electrodes where large shear forces exist because of the large gradient in electrostatic forces. Again, there appears to be no differences in the separations from group-to-group.

Polished surfaces showed two interesting features. The first was an apparent second ceramic phase possibly associated with the acicular grains noted above. These are small (0.4-4.1 volume percent) sharply defined regions which stand out against a

much more uniform background of (presumably) CPN-17. This feature correlates strongly to the state-switching phenomenon (see Section III below). The second feature is a dramatic increase in porosity near the electrodes; i.e., an average porosity of ~ 6% in the bulk material and an average porosity of ~ 30% in the electrode region.

Polished and etched surfaces revealed one unusual feature. There appear to be small grains which are more resistant to etching. These grains may be associated with the acicular grains noted above.

This microstructural study did not reveal any differences among groups of multilayers which could account for the large differences in dielectric behavior except as noted above. It did suggest several possibilities for the overall low breakdown strength in all of the groups.

Biggers, Inc. has also completed a second structural study on devices being prepared by ATC under the present contract. This study examined whether or not it was better to dice multilayers before or after binder burnout.

Multilayers are usually produced in sets from larger sheets of tape-cast material. The layers are added one at a time alternating with silk-screening of electrodes. After all the layers are added, the devices can be cut apart (diced) either before or after a prefiring.

Two groups of devices were prepared and taken through a complete, identical firing schedule, the only difference being that one group was diced in the green state; the other was prefired before dicing. The diced green state devices were significantly inferior to prefired samples in that they often showed complete layer separations at the boundary between ceramic and electrodes. There were none of these separations in the prefired group.

The study also showed two other types of defects with equal occurrence in both groups. These were regions of delaminations at the electrodes and significant porosity. Delaminations are different from the complete separations noted above only in that

they are much smaller and confined to regions of the ceramic-electrode interface. The presence of both these defects in all the samples shows that much better control of the tape-casting and stacking procedures will have to be maintained.

II. Thermal Properties and Heat Flow Models

For two practical reasons, a significant effort has been devoted to studying the thermal properties and heat flow mechanisms in multilayer capacitors (MLC's) of CPN-17. Since greater heat flow occurs parallel to the layers because of the presence of the metal electrodes, the heat flow properties could affect the geometry design of MLC's; and second, the rate of charging and discharging could be limited by thermal constraints more than electrical constraints if the various heating sources in the MLC's cause a large enough temperature rise to change the MLC properties significantly.

The first step in this analysis was measurements of the thermal conductivity of multilayers (Quarterly Report of 7/3/86) in directions both perpendicular and parallel to the electrode planes (i.e., "transverse" and "longitudinal" measurements respectively). From these measurements, it is possible to determine the separate contributions to the thermal conductivity of both the dielectric material and the electrodes. As expected, the longitudinal thermal conductivity is significantly larger than the transverse because of the presence of the metal electrodes. Other conclusions are that platinum electrodes have significantly better thermal conductivity than ternary electrodes, and that doubling (or tripling) the electrode thickness can significantly increase the longitudinal thermal conductivity.

Next a heat-flow model of an MLC was developed (Interim Report of 8/8/86) and a computer program written so that all the independent variables involved could be independently controlled. These variables include the lengths and widths of the electrodes, the size of the pullback region (no electrodes), and the thicknesses of the electrodes and the dielectric layers. It was

assumed that the edges of the MLC were anchored at 77 K and that only the longitudinal heat flow contributed to heat dissipation. The heat source was unspecified as to origin, but was assumed to occur uniformly within the MLC for some short specified times at a given magnitude. Under these various conditions, the temperature at the center of the MLC was calculated as a function of time both during and after the heat pulse.

One of the central conclusions of the study (Interim Report of 9/12/86) is shown in Fig. 1 where the magnitude of the power input was changed with all other variables held constant. The resulting curves show that no matter what the size of the heating, it takes on the order of 5-10 secs for the center temperature to cool back to near its starting temperature; i.e., under the conditions for which the model is derived, the cycle time will be limited by thermal considerations rather than electrical. If the magnitude of the heating in the real multilayers turns out to be much smaller than the numbers chosen in the study, then it might be possible to have some initial number of closely spaced cycles at the beginning, but eventually the temperature will build up to the point where the dielectric properties change significantly, at which time 5-10 secs of off-duty time will be required.

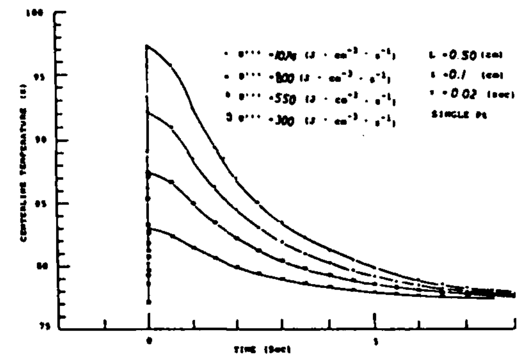

Figure 1. Centerline temperature of an MLC for various initial heat inputs.

Other results from the study are more qualitative. In order to minimize the cycle time, the electrodes should be as thick as possible, the length of the electrodes and length of the pullback region should be a short as possible and the dielelctric layer thickness as thin as possible. This argues for capacitors with many thin dielectric layers and a small electrode area.

A different assumption in the model which could alter the results of the study is the assumption that some heat will flow

in the transverse direction also. Since this is an extra path for heat loss, the longitudinal study above should be considered the worst case. At present, further studies are being made to measure the transverse heat flow across a multilayer into liquid nitrogen. The results of these studies will be reported in the future.

Finally, one source of possible heating, the electrode resistance, can be quantified before the final dielectric properties of MLC's are measured. The data on these measurements is presented in the Interim Report of 10/22/86. MLC's with both platinum and ternary electrodes were cut to expose all the electrodes at each end. The resistance of the electrodes was measured at 77 K and found to be ohmic over a wide current range. Under extremely severe conditions (maximum charge storage, short discharge times and unfavorable geometries) the temperature could be calculated to be no more than rise 1.6 K.

III. Dielectric Properties

The dielectric material used to make the energy-storage MLC's has complex dielectric properties which should be understood in order to manufacture the best possible system. In particular, the "state-switching" phenomenon as illustrated in Fig. 2 has a large effect on the energy storage properties. To review, "state-switching" is a sudden large jump (an order of magnitude) in dielectric constant ε when the E-field reaches a value of 200-300 kV/cm. It is possible the effect is a measurement artifact (i.e., a partial breakdown which lowers the voltage across the device), although

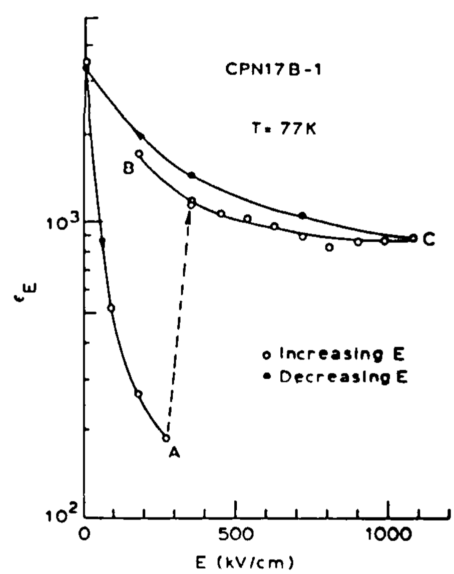

Figure 2. "Switched-State" effect in CPN-17. The arrows indicate the order in which measurements were made.

there is circumstantial evidence to indicate the effect is <u>not</u> a breakdown. Equipment has been purchased so that in the furture the voltage across a sample can be monitored directly, so there will be no ambiguity about this effect.

The material being used in this program is the pyrochlore $(Cd_{.83}Pb_{.17})_2Nb_2O_7$ (CPN-17; i.e., 17% Pb on the A-site). An understanding of this material means investigating other members of the same family, in particular, the end-member CPN-0, (i.e., $Cd_2Nb_2O_7$). The results of these investigations are in the Quarterly Report dated 10/6/86.

One explanation of the dielectric properties which has emerged is that there are two or more mechanisms in the material each contributing to ε. First, there are apparently at least two transitions in CPN-0 as shown by two peaks in the ε-T curve, the major peak at 188 K and a minor peak at ~ 80 K. As T_a substitutions are made on the B-site, the major peak shifts down in temperature while the minor peak does not shift. Lead substitutions on the A-site also shift the major peak lower in temperature and simultaneously raise ε at the peak. The maximum dielectric constant for the system occurs when the primary peak has been lowered at 80 K, implying a co-operative behavior between the mechanisms which cause the two peaks.

This review is reinforced by the behavior of the dielectric constant peaks in large E-fields. In particular, the dielectric constant of CPN-17 has two peaks moving apart in temperature at large increasing fields, as if the two components are being affected differently.

Since the present contract is a development contract, it will not be possible to pursue these dielectric studies further other than a minimal investigation of the "switched-state" if it is duplicated. Future dielectric measurements will be used only to confirm that $\varepsilon(T,E)$ has not been degraded by changes in other processing parameters.

From the groups of MLC's discussed in Section I above, it was noted that devices from certain groups went into a "switched-state" while no devices from other groups ever did.

There appear to be certain correlations between switching and geometry and microstructure differences among the groups. These are detailed in the Interim Report of 10/24/86. The geometry correlations for the appearance of switching are a low value of the ratio of transverse pullback lengths to cover plate thickness and a low value of the ratio of active to inactive layers in the transverse plane. The microstructure correlation for switching is that a low value of a secondary minor phase was necessary. These correlations will strongly affect the design of future MLC's.

IV. Breakdown Program

In the near future a large number of sample MLC's will be analyzed to breakdown at 77 K. In order to facilitate these measurements, an automated system has been built for computer-controlled dielectric constant and breakdown voltage measurements (Interim Report 12/30/86). The system allows two modes of operation: (1) Large voltage steps followed by a measurement of ε when the voltage is constant, and (2) A constant ramp rate of voltage. In both cases, the voltage across the sample is continuously monitored to observe breakdown. Dielectric constant measurements are performed by calibrating the offset signal of a bridge against capacitance and measuring the offset signal with a lock-in amplifier. The entire system provides a core of hardware and software which can be modified for lifetime and duty-cycle testing planned in Task V of this program.

V. Future Plans

At the present, the program is behind schedule. Task I should have been completed by the end of December 1986. This task involves the production and testing of multiple sets of multilayers which encompass a large number of variations in source powders, additives, processing (time-temperature) parameters, electrode variations and geometry variations to improve breakdown strength. The microstructure and room-temperature breakdown properties of these MLC's sets are to be correlated

with the parameter variations and at least four sets of MLC's will be made (Task I-D) with the highest projected breakdown strengths. These sets cannot be made until all the other data from Task I is analyzed. American Technical Ceramics has not yet made all of the sets of parameter variations, nor has Biggers, Inc. completed the testing on the sets which have been made.

Specifically, the sets which have not yet been completed are the sets for geometry variations (Task I-B) and the sets with dopants (Task I-C, #2). The MLC's with geometry variations have been tape-cast and assembled, but not fired, and CPI has been informed they will be finished when a firing study is completed. The sets with dopants have not been made because Biggers, Inc. has insufficient knowledge at this time to predict doping candidates and concentration levels, and in fact there is some question in their mind as to the necessity for doing this particular study. This question is under active review and will be decided shortly.

Biggers, Inc. has completed some important microstructural studies which are detailed in Section I of this report and the oxide compound composition studies are nearly complete. Microstructural studies of pellets under various time/temperature firing conditions are also nearing completion and the results of this study will allow other multilayer sets to be fired under the best conditions in order to perform breakdown and insulation resistance testing at room temperature.

Even though the contract is behind schedule at this point, the quality of the products will not be sacrificed. Every effort will be made to complete the contract within the projected two-year span. The goal is to make MLC's with the highest possible breakdown strength at cryogenic temperatures. These early studies are the key to this goal, and neither the studies nor the goal will be compromised. Timely completion of the contract depends at this point on how quickly the subcontractors can complete their tasks.

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